

Identification of Flavor Constituents in Carbonyl, Non-Carbonyl Neutral and Basic Fractions of Aqueous Smoke Condensates†

Kazuko KIM, Tadao KURATA and Masao FUJIMAKI

*Department of Agricultural Chemistry, Faculty of Agriculture,
The University of Tokyo, Tokyo*

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Carbonyl, non-carbonyl neutral and basic fractions obtained from commercial aqueous smoke condensates were separated by GC and/or silica gel column chromatography.

Ninety-eight constituents were identified (thirty-one compounds were not previously reported in smoke condensate) and twenty-two were tentatively identified on the basis of t_R of GC, IR, MS (GC-MS) and NMR data.

The yields of all the smoky aroma constituents (four aliphatic alcohols, five aliphatic ketoalcohols, six aliphatic ketones, twenty cyclic monoketones, three cyclic diketones, ten acids, two esters, twelve lactones, nine furan derivatives, six N-compounds, four aromatic hydrocarbons, two aromatic alcohols, nine aromatic carbonyls, twenty-four phenols and phenol ethers and five pyrocatechols) detected in commercial wood vinegar were estimated.

In a previous paper,¹⁾ it was concluded that the characteristic smoky odor was largely due to the phenolic fraction, consisting of phenolic and dicarbonyl compounds, and that the monocarbonyl and non-carbonyl neutral fractions as well as the basic fraction, having burnt or fragrant sweet aromas, might modify the monotonous smoky aroma of the phenolic fraction.

Though most aroma constituents in the phenolic fraction have been identified, those in carbonyl, non-carbonyl neutral and basic fractions have not been completely investigated. Therefore, the authors investigated aroma compounds in these three fractions.

EXPERIMENTAL

Carbonyl, non-carbonyl neutral and basic fractions used in this investigation were prepared by the methods described in the previous paper. Equipment and procedures used for the isolation and identification of compounds were also the same as described in the previous paper. In this paper, if necessary, some peaks were isolated by repeated preparative GC using a column (3 mm × 3 m) packed with 20% carbowax

20 M or subjected to GC-MS, using a column (3 mm × 3 m) packed with 10% SE 30 coated on Diasolid L (60~80 mesh). IR spectra were recorded on a Japan Spectroscopic Model IRA-1 Grating Infrared Spectrophotometer. Identification of compounds was carried out by coincidence of IR, MS and NMR as well as gas chromatographic data with those of authentic samples or with those reported in the literature. When the amount of sample in each peak was too small, identification was made on the basis of mixtures without further isolation.

Separation of the volatile compounds of non-carbonyl neutral fraction by silica gel column chromatography

A concentrate of the volatile compounds of the non-carbonyl neutral fraction was subjected to silica gel column chromatography using hexane and ether as developing solvents, as shown in Table I.

TABLE I. SOLVENT SYSTEM USED FOR SILICA GEL COLUMN CHROMATOGRAPHY AND YIELDS OF EACH FRACTION

Fr. No.	Hexane (ml)	Ether (ml)	Yield ^{a)} (mg)
I	200	0	111
II	99.5	0.5	498
III	247.5	2.5	1478
IV	196	4	835
V	192	8	579
VI	184	16	555
VII	Methanol		4824

^{a)} Not entirely solvent-free.

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RESULTS AND DISCUSSION

Carbonyl fraction

A gas chromatogram of the carbonyl fraction is shown in Fig. 1. Peaks on a rechromatogram obtained using SE 30 were numbered -1, -2 *etc.* Peaks No. 16, 17, 19, 20, *etc.* consisted of more than two compounds.

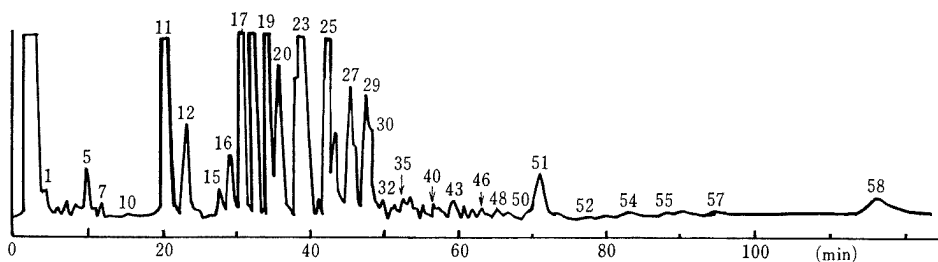


FIG. 1. Gas Chromatogram of the Carbonyl Fraction Obtained by GC-MS.

Column temp.: 70→190°C (2°C/min).

Carrier gas: He, 1.0 kg/cm².

11) cyclopentanone, 15) cyclohexanone, 17-1) 2-cyclopentenone, 18) 2-methyl-2-cyclopentenone, 19) furfural, acetolacetate, 20-1) 2-acetylfuran, 22) 3-methyl-2-cyclopentenone, 23) 2,3-dimethyl-2-cyclopentenone, 25) 5-methylfurfural.

Peak 12 was identified as methylcyclopentanone on the basis of the following data; IR ($\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1700 (C=O)), MS (m/e : 98 (M^+)), NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ ppm: 1.15 (3H, d, CH₃), 2.10 (6H, 3CH₂)), but the position of the methyl group was not determined.

Peaks 16-1, -2, 17-2, 19-2~4, 20-2, -3, 23-4, 17 and 28 were suggested to be 2-cyclopentenone homologues, because they showed the same MS fragmentation patterns (M^+-15 , M^+-28 , M^+-29 , M^+-43) and characteristic absorptions ($\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1700~1720 (C=O), 1580~1640 (C=C)) in the IR, corresponding to α,β -unsaturated 5-membered cyclic ketones. It is known that both the intensity and position of absorption bands due to stretching vibrations of double bonds are specifically influenced by the location of substituents, but are only slightly influenced by their type.^{2~3)} The 2-cyclopentenone homologues listed in Table II were identified by comparison of their t_R of GC, IR, MS or

NMR data with those standard samples* (3-methylcyclopentenone, 3-propyl and 2,3-dimethyl) or with reported data (unsubstituted, 2-methyl, 2-ethyl-3-methyl), for instance; IR ($\nu_{\text{C}=\text{C}}$ cm⁻¹: homologue with no substituent (1580, weak), 2-substituted derivatives (1640, weak), 3- (1620, strong) and 2,3- (1640, very strong)), NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ ppm 2-CH₃ (2.1~2.0), 3-CH₃ (1.8~1.6), 2=CH (3.94), 3=CH (2.5~

3.0)).

The other carbonyl constituents were identified as shown in Table III.

Peaks 23-2, 26, 29 and 51-3 were identified as benzaldehyde, 5-methyl-2-acetylfuran, acetophenone and 1-indanone, respectively, by coincidence of their IR, MS and NMR data with those of authentic samples.

Peaks 32 and 35, which had the same molecular weight (MS m/e : 134 (M^+)), were identified as *m*-methyl and *p*-methyl acetophenone by coincidence of IR data with the published values.⁴⁾

Peaks 48, 50, 54, 55 and 56 gave the same parent peak in MS (m/e : 146 (M^+)) and IR spectra similar to 1-indanone. On the basis of t_R of GC, MS or IR, NMR data, peaks 48, 50 and 54 were identified as 2-methyl,* 3-methyl* and 6-methyl-1-indanone, respectively, but 55 and 56 could not be identified

* These synthetic samples were presented by Mr. H. Shigematsu.

TABLE II. IR, MS AND NMR DATA FOR 2-CYCLOPENTENONES

P. No.	Compound	t_R of GC ^{b)}	IR (ν_{\max}^{film} cm ⁻¹)	MS (m/e)	NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ ppm)
16-1	5-(or 4-)Methyl-2-cyclopentenone ^{a)}	24.5	1710, 1580/1340 1420, 945	96 (65), 95 (31), 81 (100) 68 (23), 67 (76), 53 (77)	1.14 (3H, d), 2.30 (2H), 2.80 (1H), 6.08 (1H), 7.08 (1H)
-2	2,5-Dimethyl- ^{a)}	"	1710, 1645/1335, 1440, 1015, 1100	110 (53), 95 (87), 82 (21) 67 (100), 41 (38) 39 (41)	1.14 (3H, d), 1.72 (3H), 2.40 (2H), 2.80 (1H), 7.08 (1H)
17-2	2,4- ^{a)}	25.6	1705, 1640/1330 1060, 1440	110 (41), 95 (44), 82 (33) 67 (100), 41 (51), 39 (43)	
19-2	2-Ethyl-5-methyl- ^{a)}	31.5	1710, 1640/1440, 1380, 1330, 1020	124 (65), 109 (80), 81 (100) 79 (40), 67 (24), 41 (25)	
-3	2-Ethyl-4-methyl- ^{a)}	"		124 (40), 109 (39), 96 (100) 95 (42), 81 (59), 79 (72)	
-4	2-Ethyl-2-cyclopentenone	"		110 (52), 82 (100), 69 (53) 68 (14), 67 (34), 54 (43)	1.08 (3H, t), 2.12 (2H), 2.30 (2H), 2.52 (2H), 7.13 (1H)
20-2	3,5-Dimethyl-2- ^{a)}	34.2	1700, 1625/1440, 1455, 1000, 1245	110 (66), 95 (28), 81 (12), 68 (17), 67 (100), 53 (63)	1.12 (3H, d), 2.09 (3H), 2.30 (2H), 2.70 (1H), 5.82 (1H)
-3	3,4- ^{a)}	"	1700, 1620/1428, 1170, 1380, 830	110 (49), 95 (33), 82 (11), 81 (24), 68 (12), 67 (100)	
23-4	2,3,5-Trimethyl-2-cyclopentenone ^{a)}	35.9	1700, 1650/1330, 1380, 1440, 1000	124 (51), 110 (46), 109 (62), 96 (10), 95 (100), 81 (48), 67 (17)	1.12 (3H, d), 1.61 (3H) 2.00 (3H), 2.30 (2H), 2.70 (1H)
-5	Unknown	"		124 (73), 109 (52), 96 (95), 95 (16), 82 (28), 81 (53), 67 (100)	
25-3	2-Ethyl-3-methyl- ^{a)}	38.2	1700, 1645/1390, 1440, 1055, 1180	124 (100), 109 (55), 95 (37), 81 (85), 67 (93), 53 (40)	0.97 (3H, t), 2.02 (3H) 2.24 (6H)
27	3-Ethyl-2-cyclopentenone	42.0	1710, 1620/1180, 1440, 1270	110 (90), 81 (100), 67 (55), 53 (70), 41 (40), 39 (55)	1.21 (3H, t), 2.4 (6H), 5.82 (1H)
28	3-Ethyl-2-methyl-2-cyclopentenone	42.8	1710, 1690, 1645/ 1070, 1300, 1345	124 (92), 109 (100), 95 (91), 81 (71), 67 (86), 41 (25)	
32-2	3- <i>n</i> -Propyl-2-cyclopentenone	46.8		124 (90), 109 (40), 96 (90), 95 (45), 81 (100), 67 (60)	

^{a)} Positions of the substituents were not definitely determined.^{b)} The retention times were measured under the following conditions: Column temp., 70~200°C (2°C/min); carrier gas, He; flow rate, 30 ml/min.

because the amounts present were insufficient.

Peaks 46, 51-1 and 51-2 appeared to be nitrogen-containing compounds because of their parent ion peaks and the abundance of even mass number fragments in MS. Peak 46, which showed the presence of m/e 94 ($M^+ - \text{CH}_3$) and 66 ($M^+ - \text{COCH}_3$), was identified as α -methylpyrrolketone by coincidence of the IR with published references. Peaks 51-1 and 51-2 were identified as α -formylpyrrole and ethylpyrrolketone by coincidence of the MS spectra with reported data.⁵⁾

Non-carbonyl neutral fraction

Non-carbonyl neutral fraction obtained from a mixture of six types of wood was separated into seven fractions by silica gel column chromatography. Though all the fractions were analysed by GC-MS, fraction 1, which had a petroleum-like odor and was present in only a small amount, was not investigated. Peaks 29, 34, 44, 47, 48 and 49 were well separated. All the compounds in fractions II and VI were found in the other

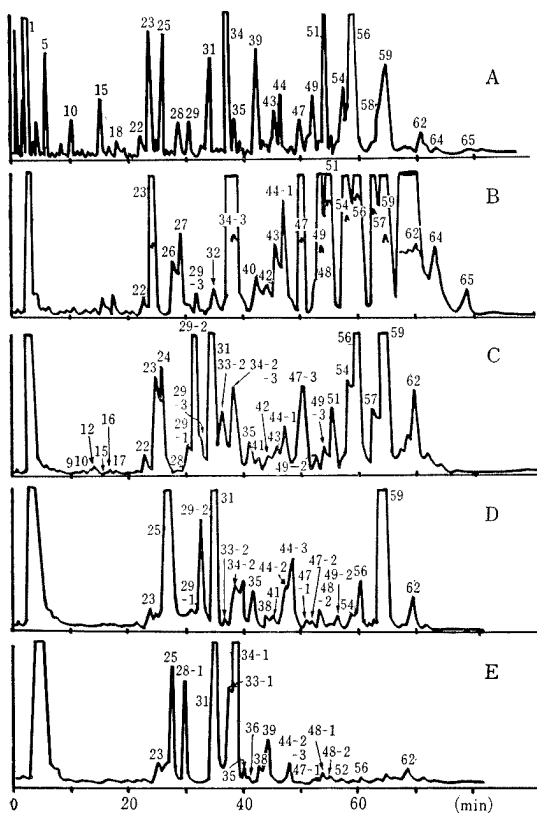


FIG. 2. Gas Chromatograms of the Non-carbonyl Neutral Fraction (A, the whole; B, fraction III; C, fraction IV; D, fraction V; E, fraction VII) Separated by Silica Gel Column Chromatography.

Column temp.: 70→200°C (2°C/min).

Carrier gas: N₂, 30 ml/min.

2) 2-butanone, 3) methylpropionate, 10) ethylbenzene, 11) *p*-xylene, 12) *m*-xylene, 16) *o*-xylene, 15) 3-pentanone 18–1) *n*-amylalcohol, 22) cyclohexanone, 23) 2,5-dimethyl-2-cyclopentenone, 24) 2,4-dimethyl-2-cyclopentenone, 25) 2-methyl-2-cyclopentenone, 26~27) 2-ethyl-5-methyl-2-cyclopentenone, 2-ethyl-4-methyl-2-cyclopentenone, 28–1) furfural, 29–1) 2-ethyl-2-cyclopentenone, 29–2) 3,5-dimethyl-2-cyclopentenone, 31) 2-acetylfuran, 3,4-dimethyl-2-cyclopentenone, 33–1) 3-methyl-2-cyclopentenone, 33–2) 2,3,4-(or 5)-trimethyl-2-cyclopentenone, 34–1) 2,3-dimethyl-2-cyclopentenone, 34–2) 5-methyl-2-furfural, 34–3) 2-methylfuroate, 35–1) 5-methyl-2-acetylfuran, 38) 3-ethyl-2-cyclopentenone, 43) 1,2-dimethoxybenzene, 47–3) 1,2-dimethoxy-4-methylbenzene, 51–3) 1,2-dimethoxy-4-ethylbenzene, 51–2) 2,6-xyleneol, 54) 4-methylguaiacol, 56) *p*-cresol, 57) 4-ethylguaiacol, 58) *m*- and *p*-cresol, 59) 2,4-xyleneol, 60) 4-propylguaiacol, 61) 2,3-xyleneol, 62) 3,5-xyleneol, 63) 4-vinylguaiacol, eugenol, 64) 3,4-xyleneol, 2,3,5-trimethylphenol, 65) 3-ethyl-5-methylphenol, *cis*-isoeugenol.

fractions.

Identification of peaks 18, 39, 44–1~3, 47–3, 48–1, 49–1~3 and 51–1, –3 was achieved as shown in Table IV.

Peak 18 was identified as furfurylmethyl-ether by coincidence of the MS⁶⁾ and on the basis of NMR data.

Peaks 39, 44–1, 44–3, 49–2 and 48–1 were suggested to be 2-substituted 2-butenolide homologues since they showed two common absorptions at 1660 (C=C) and 1750~60 (O–C=O) without splitting caused by Fermi resonance in the IR. Both peaks 44–1, and 49–2 showed the same parent ion (*m/e* 124) and a common fragmentation pattern (*m/e*: 96, 82, 40, 39), but the stability of the parent ion peak was higher in peak 44–1 than in 49–2. Peak 44–1 was identified as 4-ethylidene-2-methyl-2-butenolide (4-hydroxy-2-methyl-hexa-2,4-dienoic acid γ -lactone) by comparison of the NMR data ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$: 1.95 (3H, s, =C–CH₃), 1.92 (3H, d, *J*=7.5 Hz, =C–CH₃), 4.99 (1H, q, *J*=7.5 Hz, =CH–Me)) with those of 2-butenolide. As peak 49–2 showed the presence of a vinyl group in its IR spectrum (990, 910 cm^{–1}), it was assumed to be methylvinyl-2-butenolide. Similarly, peaks 44–2 and 44–3, which showed the same parent peak at *m/e* 126 on their MS spectra, were identified as 2-ethyl-4-methyl-2-butenolide and 4-ethyl-2-methyl-2-butenolide, respectively, on the basis of their NMR data; 44–2 (1.38 (3H, d, *J*=7 Hz, CH₃), 1.05 (3H, t, *J*=7.5 Hz, CH₃), 2.25 (2H, q, *J*=7.5, –CH₂–Me), 4.8 (1H, –O–CH), 6.95 (1H, =CH)), 44.3 (1.86 (3H, =C–CH₃), 1.0 (3H, t, *J*=7.5 CH₃), 1.68 (2H, m, –CH₂–Me), 4.72 (1H, CH), 6.94 (1H, =CH)). The latter assignment was supported by agreement of the IR values with reported data.³⁾ Peak 39 was identified as 2,4-dimethyl-2-butenolide on the basis of its IR, MS and NMR data: MS (*m/e*: 112 (M⁺)), NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$: 1.43 (3H, d, *J*=7, CH₃), 1.87 (3H, =C–CH₃), 4.8 (1H, m, CH), 6.85 (1H, m, =CH)). Peak 48–1, which gave a parent peak at *m/e* 126, was identified as 2,3,4-trimethyl-2-butenolide because the IR spectrum agreed with reported data.⁷⁾ Though

TABLE III. IR, MS AND NMR DATA FOR OTHER CARBONYL COMPOUNDS

P. No.	Compound	t_R of GC	IR ($\nu_{\text{max}}^{\text{film}}$ cm^{-1})	MS (m/e)	NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ ppm)
23-2	Benzaldehyde	38		106 (100), 105 (98), 77 (99), 52 (11), 51 (39), 50 (20)	
26	2-Acetyl-5-methyl-furan	42		124 (36), 109 (100), 53 (32), 43 (24)	2.34 (3H, s), 2.38 (3H, s), 6.07 (1H), 6.91 (1H)
29	Acetophenone	44	1680, 1270, 760,	120 (40), 105 (100), 77 (60), 690, 1360, 1450, 956	
32	<i>m</i> -Methyl-acetophenone	48	1680, 1275, 1360,	51 (27), 43 (62), 39 (25), 134 (45), 119 (100), 91 (98), 780, 685, 1190, 1600	
35	<i>p</i> - " "	49.5	1680, 1270, 1360,	65 (30), 51 (20), 43 (30), 810, 1600, 1450	
48	2-Methyl-1-indanone	59.2		146 (100), 131 (98), 118 (40), 115 (41), 105 (75), 91 (20),	
50	3- " "	61.0		146 (100), 131 (98), 118 (40), 115 (41)	1.40 (3H, d), 2.62 (2H), 7.37 7.64 (4H)
51-3	1-Indanone	62.0	1710, 755, 1280, 1610, 1035	132 (100), 104 (96), 103 (50), 78 (38), 77 (37), 76 (30),	2.62 (2H), 3.12 (2H), 7.37 7.64 (6H)
54	6-Methyl-1-indanone	67.0	1710, 777, 1438, 1280, 1610, 1110	146 (100), 131 (40), 118 (68), 117 (76), 115 (34), 103 (25)	
55	Unknown	69.3		146 (100), 118 (75), 117 (75), 115 (26), 108 (27), 91 (43)	
56	"	70.2		146 (100), 118 (75), 117 (90), 115 (34), 103 (14), 91 (26)	
46	2-Acetylpyrrole	55.0	1640, 1400, 3280, 754, 1420, 1120, 1040, 920	109 (80), 94 (100), 66 (55), 54 (34), 43 (30), 39 (40)	
51-1	2-Formylpyrrole	62.0		95 (100), 94 (75), 66 (65), 39 (50)	
-2	α -Ethylpyrrol-ketone	"		123 (40), 94 (100), 66 (25), 39 (30)	
58	Unknown	80.3	1620, 1710, 1238, 1177, 748, 1020, 930, 885	162 (100), 134 (12), 133 (19), 120 (80), 106 (83), 91 (46),	

peaks 47-1, 47-2, 48-2 and 52 were suggested to be lactones by MS data (47-1: 112 (M^+), 47-2: 140 (M^+), 48-2: 140 (M^+), 52: 140 (M^+)), they were not identified because they were present in such small amounts.

Peaks 47-3 and 51-3 were identified as 4-methyl- and 4-ethyl-1,2-dimethoxybenzene by comparison of t_R of GC, IR and MS spectra with reported data.⁸⁾ They had been obtained from pyrolysis products of wood.

Peaks 49-1 and 51-1 were identified as benzylalcohol and phenylethylalcohol by the same methods as peak 47-3.

Peaks 51 through 66 were identified as mainly phenolic compounds by GC-MS. Peak 49-3 was tentatively identified as 3-or 6-

methylguaiacol on the basis of the following data; MS (m/e : 138 (M^+)), IR ($\nu_{\text{max}}^{\text{film}}$ cm^{-1} : benzene ring (1628, 1490, 1485), 1,2,3-substituted (765, 730), OH (1220)), NMR (δ : 2.25 (3H, s, Ar-CH₃), 3.75 (3H, s, OCH₃), 6.56 (2H), 6.88 (1H)).

Basic fraction

A gas chromatogram of the basic fraction obtained from oak A* is shown in Fig. 3.

Peaks 15, 20 and 21-3 were identified as pyrazine, 2-methyl, and 2,5- (or 2,6-)dimethylpyrazine, respectively, by comparison of their t_R of GC and MS data with those of authentic

* *Quercus serrata*.

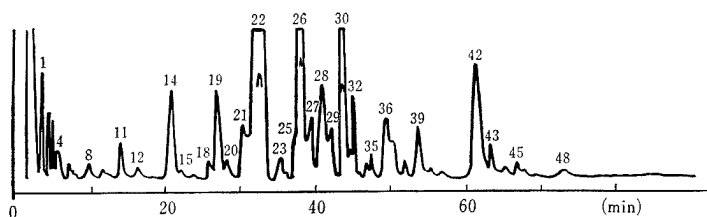


FIG. 3. Gas Chromatogram of the Basic Fraction Obtained from Nara.

Column temp.: 70→180°C (2°C/min).

Carrier gas: N₂ 30 ml/min.

1) acetone, methanol, 2) ethanol, 3) 2-butanone, 4) 2-pentanone, 5) diacetyl, propanol, 11) allyl alcohol, 12) allylmethylketone, 14) cyclopentanone, 19) acetoin, 21) acetol, pentan-3-on-2-ol, 22) 2-cyclopentenone, butan-2-on-1-ol, 2-methyl-2-cyclopentenone, 26) furfural 28) 2-acetylfuran, 29) 2,4-hexadione, 30) 3-methyl-2-cyclopentenone, 31) 2,3-dimethyl-2-cyclopentenone, 32) 5-methyl-2-furfural, 33) 5-methyl-2-acetylfuran, 36) 2,4-dimethyl-2-butenolide, 37) γ -butyrolactone, 38) β -angelicalactone, 42-2) guaiacol, 47) 4-methylguaiacol, 48) phenol.

TABLE IV. IR, MS AND NMR DATA FOR AROMA CONSTITUENTS OBTAINED FROM THE NON-CARBONYL NEUTRAL FRACTION

P. No.	Compound	t_R (min)	IR ($\nu_{\text{max}}^{\text{film}}$ cm ⁻¹)	MS (m/e)	NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ ppm)
18	Furfurylmethyl- ether			112 (28), 81 (100), 53 (51), 41 (30), 39 (26)	3.17 (3H, s), 4.19 (2H, s), 6.12 (2H), 7.21 (1H, m)
39	2,4-Dimethyl-2- butenolide	42.7	1755, 758, 1080, 1100, 1030, 1000, 1320	112 (66), 97 (36), 69 (100), 43 (45), 41 (68), 39 (34)	1.43 (3H, d), 1.87 (3H), 3H), 4.8 (1H), 6.85 (1H)
44-1	4-Ethylidenyl-2- methyl-2- "	46.8	1760, 985, 1050, 750, 1080, 1255, 1435, 1330	124 (100), 82 (89), 68 (85), 67 (39), 40 (64), 39 (49)	1.95 (3H, s), 1.92 (3H, d), 4.99 (1H, q), 6.85 (1H, s)
-2	2-Ethyl-4-methyl- 2- "	"		126 (24), 83 (63), 55 (100), 43 (50), 41 (23), 39 (32)	1.05 (3H, t), 1.38 (3H, d), 4.8 (1H), 6.95 (1H)
-3	4-Ethyl-2-methyl- 2- "	"	1760, 1085, 1028, 960, 1320, 1350, 1440, 1056	126 (43), 97 (98), 69 (93), 57 (31), 41 (100), 39 (45)	1.0 (3H, t), 1.68 (2H, q), 1.86 (3H), 4.72 (1H), 6.94 (1H)
47-1	Unknown	50.0		112 (38), 83 (76), 67 (27), 55 (100), 53 (20), 39 (46)	
-2	"	"		140 (47), 125 (14), 111 (63), 83 (97), 67 (48), 55 (100)	
48-1	2,3,4-Trimethyl- 2-butenolide	52.6	1745, 1677, 1045, 1056, 1320, 1438, 765	126 (26), 97 (40), 83 (60), 55 (100)	
-2	Unknown	"		140 (53), 97 (100), 69 (89), 54 (23), 43 (70), 41 (67)	
49-2	Methylvinyl-2- butenolide	53.5	1760, 797, 990, 910, 1025, 1345, 1605, 1650	124 (66), 82 (100), 68 (83), 56 (48), 40 (43), 39 (43)	
50	Unknown	54.3		82, 68, 39, 40, 124, 96	
49-1	Benzylalcohol	53.5		108 (87), 107 (67), 91 (15), 79 (100), 77 (57), 51 (30)	
51-1	Phenylethylalcohol	54.9		122 (16), 92 (59), 91 (100), 65 (18)	
49-3	3-(or 6-)Methyl- guaiacol	53.5	1270, 1485, 1495, 1220, 1080, 1095, 1440, 765	138 (100), 123 (90), 95 (47), 77 (55)	2.25 (3H, s), 3.75 (3H), 6.56 (2H), 6.88 (1H)

TABLE V. IR, MS AND NMR DATA FOR AROMA CONSTITUENTS OBTAINED FROM THE BASIC FRACTION

P. No.	Compound	t_R (min)	IR ($\nu_{\text{max}}^{\text{film}}$ cm^{-1})	MS (m/e)	NMR ($\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ ppm)
15	Pyrazine	17.2		80 (100), 53 (44), 26 (30)	
18-2	2-Methyltetrahydro-furan-3-one	19.1	1755, 1060, 1160, 1118, 1018, 760, 1445, 1405,	100 (40), 72 (30), 43 (100), 42 (42), 41 (44)	
20	Methylpyrazine	20.7		94 (100), 67 (57), 43 (22), 42 (20)	
21-3	2,5-(or 2,6-)Di-methylpyrazine	24.6		108 (100), 107 (87), 53 (47), 40 (45), 39 (46)	
22-4	2-Acetyltetrahydro-furan-3-one	26.3		114 (-), 71 (85), 43 (100), 41 (48), 27 (40)	
24	Unknown	28.0		100 (77), 71 (24), 70 (20), 45 (21), 42 (100), 41 (56)	
25	Propan-2-on-1-ol	29.0		102 (10), 71 (100), 43 (82), 41 (80), 39 (31), 31 (51)	1.04 (3H, q, $J=7$ Hz), 1.74 (2H, m), 2.46 (2H, t, $J=7$), 4.16 (2H, s), 3.6 (1H)
39	2-Methyl-2-butenolide	46.8	1750, 1050, 1080, 1210, 828, 1348, 1440	98 (96), 69 (100), 45 (31), 43(33), 40 (31), 39 (80)	1.92 (3H), 4.68 (2H, d, $J=2.5$), 7.05 (1H, m)
42-1	3,4-Dimethyl-2- "	53.8	1740, 1069, 945, 1286, 1155, 1166, 1640, 1440		
43	23- "	54.8	1745, 1025, 1075, 1675, 755, 1319, 1440, 1383		

TABLE VI. FLAVOR CONSTITUENTS IN WOOD VINEGAR LIQUOR OBTAINED FROM OAK A^{a)}

Compound	Yield (mg %)	Odor	Methods of identification			
Aliphatic alcohols						
methanol				GC,	MS	
ethanol				"	"	
allyl alcohol		Stone-leek like		"	"	
<i>n</i> -amyl alcohol			IR,		MS,	NMR
Aliphatic keto alcohols						
propan-2-on-1-ol	0.6	Stone-leek like			MS	
butan-2-on-1-ol	0.4				MS,	NMR
pentan-2-on-1-ol	0.4				MS,	NMR
butan-3-on-2-ol	0.6		IR,	GC,	MS,	NMR
pentan-3-on-2-ol	0.6				MS,	NMR
Aliphatic ketones						
acetone				GC,	MS	
2-butanone				"	"	
2-pentanone				"	"	
allylmethylketone ^{b)}				"	"	
diacetyl				GC,	MS	
2,4-hexadione	1.6			"	"	
cyclic ketone	1.6					
cyclopentanone	11		IR,	GC,	MS,	NMR
methylcyclopentanone	1.7		IR,		MS,	NMR

Compound	Yield (mg %)	Odor	Methods of identification			
cyclohexanone				MS		
2-cyclopentenone	169	Grassy potato-like	IR,	MS,	NMR	
2-methyl-2-cyclopentenone			"	"	"	
3-methyl-	8.4	Somewhat sweet, grassy	GC,	IR,	MS,	NMR
4-(or 5-)methyl- ^{b)}			"	"	"	
2,3-dimethyl- ^{b)}	12.4	Grassy and bitter	GC,	"	"	"
2,4- ^{b)}	6.9	Somewhat grassy	"	"	"	"
2,5- ^{b)}	11.5	"	"	"	"	"
3,4- ^{b)}	3.2	"	"	"	"	"
3,5- ^{b)}	12.5	"	"	"	"	"
2,3,4-(or 5-)trimethyl- 2-cyclopentenone ^{b)}	0.6		"	"	"	
2-ethyl-2-cyclopentenone ^{c)}	2.5		"	"	"	
3- ^{c)}	6.0	Grassy	"	"	"	
2-ethyl-3-methyl-2- cyclopentenone ^{c)}	5.2	Mild medicine-like	"	"	"	
3-ethyl-2-methyl-2- cyclopentenone ^{c)}	1.6	"	"	"	"	
2-ethyl-4-methyl- ^{b)}	0.6	Grassy		MS		
2- " 5- " ^{b)}			IR,	MS		
3- <i>n</i> -propyl-2-cyclopente- none ^{c)}		"	GC,	MS		
3-methylcyclopenta-1,2-dione	11.2	Sweet and burnt caramel-like	IR,	MS		
3,4-dimethyl	2.2	"	"	"		
3-ethyl	2.6	"	"	"		
Acids						
acetic		Pungent	GC,	IR,	MS	
propionic		"	GC	"	"	
<i>n</i> -butyric		Rancid	"	"	"	
iso- "		Pungent	"	"	"	
<i>n</i> -valeric		Rancid	GC,	IR,	MS	
iso- "			"	"	"	
<i>trans</i> -crotonic		"	"	"	"	NMR
<i>cis</i> - "			"	"	"	"
2-pentenoic ^{b)}			"	"	"	
α -methylcrotonic ^{b)}			"	"	"	
Esters						
methylbutyrate		Floral	GC,	MS,	NMR	
acetolacetate				MS		
Lactones						
γ -butyrolactone	0.6	Somewhat bitter burnt	IR,	MS		
2-butenolide	Trace			MS		
2-methyl-2-butenolide ^{c)}	1.1	Sweet, burnt caramel-like	IR,	MS,	NMR	
4- " ^{c)}	0.3	Smoky and burnt	"	"	"	
2,3-dimethyl- ^{c)}	0.6	Spicy vanilla-like	"	"	"	
2,4- " ^{c)}	14.5	Sweet and burnt	"	"	"	
3,4- " ^{c)}	1.5	Weak sour smoky	"	"	"	
2,3,4-trimethyl-2-butenolide ^{c)}	1.5	Sweet, burnt caramel-like	"	"		
2-ethyl-4-methyl-2-butenolide ^{c)}	8.1	Burnt woody		MS,	NMR	
4- " -2- " ^{c)}			IR,	MS,	NMR	
4-ethylidene-2-methyl- 2-butenolide ^{c)}	1.0	Sweet caramel-like	IR,	MS,	NMR	
methylvinyl-2-butenolide ^{b)}	Trace	"	"	"	"	

Compound	Yield (mg%)	Odor	Methods of identification			
Furans						
furfural	259	Sweet bread-like caramel-like	GC,	IR,	MS,	NMR
5-methylfurfural	90	Sweet-spicy, warm slightly caramel-like		IR,	MS,	NMR
2-furylmethylketone	30	Powerful balsamic-sweet		"	"	"
2-(5-methylfuryl)- methylketone ^{c)}	6.8	Sweet fragrant			MS,	NMR
methylfuroate	15	Grassy acetophenone-like		IR,	MS,	NMR
furylmethylether ^{c)}					MS,	NMR
2-methyltetrahydrofuran-3-one ^{b)}					(MS)	
2,5-dimethyl- 2-acetyl	" ^{b)} " ^{b)}	"			(MS) MS	
N-Compounds						
pyrazine ^{c)}	0.2	Popcorn-like	GC,		MS	
methylpyrazine ^{c)}	0.3	"	"		"	
2,5-(or 2,6-)dimethyl pyrazine ^{b)}	0.5	"	"		"	
2-formylpyrrole ^{c)}	Trace	Burnt smoky			MS	
α -methylpyrrolketone ^{c)}	0.4	Sweet and burnt		IR,	MS	
α -ethylpyrrolketone ^{c)}	Trace	"			MS	
Aromatic compounds						
<i>o</i> -xylene	Trace	Petroleum-like	GC,		MS	
<i>m</i> - "	"	"	"		"	
<i>p</i> - "	"	"	"		"	
ethylbenzene	"	"	"		"	
benzylalcohol ^{c)}	"	Faint, nondescript odor	"		"	
phenylethylalcohol ^{c)}	"	Mild, warm, rose-honey	"		"	
1,2-dimethoxybenzene	1.9	Burnt and woody		IR,	MS	
1,2- " -4-methylbenzene	0.9	Wood vanilla-like	GC,	IR,	MS	
1,2- " -4-ethylbenzene	Trace	Sweet, woody vanilla-like	GC,	IR,	MS	
benzaldehyde ^{c)}	"	Oil of almond	GC,		MS	
acetophenone ^{c)}	3.5	Sweet floral	GC,	IR,	MS,	NMR
<i>m</i> -methylacetophenone ^{c)}	0.6	Grassy, sweet floral		IR,	MS	
<i>p</i> - "	0.6	"		"	"	
1-indanone ^{c)}	1.9	Somewhat phenolic vanilla-like	GC,	IR,	MS	
2-methyl-1-indanone ^{c)}	0.3	Mild fragrant	GC,		MS	
3- " " ^{c)}	0.3	"	"		"	NMR
6- " " ^{c)}	0.3	"	"	IR,	MS	
phenol		Pungent characteristic	"	"	"	
<i>o</i> -cresol	98	"	"	"	"	
<i>m</i> - and <i>p</i> -cresol		"	"		"	
2,3-xyleneol	24	"	"	"	"	
2,4- "		"	"	IR,	"	
2,6- "	9.3	Cresolic	"	"	"	
3,4- "	0.6	"	"	"	"	
3,5- "	2.7	"	"	"	"	
2-ethyl-5-methylphenol ^{b)}		"	"		"	
2,3,5-trimethylphenol ^{b)}		"	"		"	
3-ethyl-5-methylphenol ^{b)}		"	"		"	
guaiaicol	99	Sweet smoky and somewhat pungent	"	"	"	
3(or 6)-methylguaiaicol ^{b)}	6	Weak phenolic		"	"	NMR
4- "	33	Sweet smoky	"	"	"	
4-ethylguaiaicol	4	"	"	"	"	

Compound	Yield (mg%)	Odor	Methods of identification			
4-vinylguaiacol		Sweet smoky			MS	
4-propylguaiacol	0.6		GC,	IR,	"	
4-allylguaiacol	2.5	Woody	"	"	"	
acetovanillone	Trace		"	"	"	
2,6-dimethoxyphenol	8.9	Smoky	"	"	"	
2,6-dimethoxy-4-methylphenol	3.6	Mild heavy burnt		"	"	
" -4-ethylphenol		"		"	"	
" -4-propylphenol		"		"	"	
" -4-propenylphenol ^{a)}					"	
pyrocatechol		Heavy sweet burnt	GC,	IR,	MS	
3-methylpyrocatechol ^{a)}		"	"	"	"	NMR
4- "		"	"	"	"	"
4-ethylpyrocatechol		"		"	"	
3-methoxypyrocatechol			"	"	"	

^{a)} *Quercus serrata*.

^{b)} These compounds were tentatively identified.

^{c)} These compounds were not previously reported in smoke condensate.

samples.

Peak 25 was identified as propan-2-on-1-ol on the basis of MS and NMR data.

Peaks 39, 42-1, 43 and 44 were suggested to be 2-butenolides by their IR spectra which were similar to that of 2,4-dimethyl-2-butenolide. Peak 39 was identified as 2-methyl-2-butenolide on the basis of MS (*m/e*: 98 (M^+)) and NMR (δ : 1.92 (3H, CH_3), 4.68 (2H, CH_2), 7.05 (1H, $=CH$)). Peaks 42-1 and 43 were identified as 3,4-dimethyl and 2,3-dimethyl-2-butenolide, respectively, by coincidence of their IR and MS with reported values.⁷⁾

Peak 12 was identified as 2-methyltetrahydrofuran-3-one from MS and IR data. Peak 22-4 was tentatively identified as 2-acetyltetrahydrofuran-3-one by coincidence of the MS spectrum with reported data.⁶⁾

Most alkyl amines, aldehydes, ketones and alcohols *etc.* with low boiling points might be lost during the preparation of flavor concentrates. As important flavor constituents were thought to be higher boiling point compounds rather than lower boiling ones, the latter was not considered in detail in our study.

All the flavor constituents found in commercial wood vinegar obtained from oak A are shown in Table VI. Approximate amounts were estimated by the same methods described in the previous paper. When a

certain flavor constituent was detected in more than two fractions, however, yields indicate the total amount of the aroma constituent in each fraction. The identity of more than 90% of the flavor constituents in smoke condensate has been confirmed or tentatively identified in this paper. Furfural, 5-methylfurfural, 2-cyclopentenone, 2-methyl-2-cyclopentenone, guaiacol, 4-methylguaiacol, phenol, *o*-cresol, as well as acetic, propionic and *n*-butyric acids were the main components. Except for phenolic compounds, the more important flavor constituents seemed to be carbonyls and lactones with higher boiling points. Many alkyl-substituted 1,2-cyclopentadione and 2-butenolide homologues have sweet burnt or caramel-like odors, and may contribute considerably to an acceptable smoke flavor. The burnt odor in the whole smoky flavor was mainly presented by 2-butenolide derivatives. Furfural, 5-methylfurfural, 2-acetylfuran and acetophenone have sweet fragrant floral aromas, and they seemed to contribute to a partial softening of the heavy smoky aromas of phenolic compounds. Many 2-cyclopentenone derivatives were present in smoke condensate, but many of them have a bitter taste and odor with grassiness. Their effect on the smoke flavor was not significant. Most smoke flavor constituents found by Fiddler *et al.*⁹⁾ in a liquid smoke solution were

also detected in the wood vinegar.

Most of the phenolic compounds observed are considered to be produced by the pyrolysis of lignin in wood. Similarly, many cyclopentadiones, carbonyls, lactones, ketoalcohols and acids, some of which have been observed in pyrolysis products of carbohydrates, seem to be generated from cellulose (40~60%) and hemicellulose (15~30%) in wood.

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